Cluster Compounds

Metal-Rich, Neutral and Cationic Organotin Clusters**

*Anne F. Richards, Barrett E. Eichler, Marcin Brynda, Marilyn M. Olmstead, and Philip P. Power**

With few exceptions, isolated clusters of the heavier Group 14 elements (Si–Pb) are of the Zintl (E_n^{x-}, $x = 2$, 3, or 4)[1,2] or organically substituted, that is, E_nR_m ($n = m$ or $n > m$; R = aryl, aryl, silyl, amide),[3,4] types. A notable feature of the two classes is that they rarely display a structural or electronic correspondence to each other. This situation is particularly evident in the structures of the element-rich[5] Group 14 organo clusters E_nR_m ($n > m$) such as $Sn_8\{Si(SiMe_3)_3\}_6$,[6] $Sn_8(Ar^{Mes_2})_4$[7] ($Ar^{Mes_2} = 2,6\text{-}Mes_2C_6H_3$; $Mes = 2,4,6\text{-}Me_3C_6H_2$), $Ge_8\{N(SiMe_3)_2\}_6$,[8] $Ge_6(Ar^{Mes_2})_2$,[9] $Sn_4Ge_2(Ar^{Mes_2})_2$[9] as well as the recently reported lead clusters $Pb_{10}R^*_6$ and $Pb_{12}R^*_6$ ($R^* = Si(SiMe_3)_3$).[10] These bear little stoichiometric or structural resemblance to the common E_5^{x-} or E_9^{x-} (E = Si–Pb) Zintl ions of these elements. A number of publications have shown that Zintl ion clusters, such as E_9^{x-}, can be derivatized with transition-metal or main-group fragments with preservation of the original framework.[11–15] Nonetheless, there is only one example (the anion $[Ge_9\{N(SiMe_3)_2\}_3]^-$)[16] of a derivatized Zintl cluster that can be synthesized without use of preformed E_5^{x-} or E_9^{x-} units. No stable examples of neutral clusters with structures analogous to the Zintl ions exist at present. Similarly, knowledge of cationic clusters of the Group 14 elements is extremely limited. For example, cationic Zintl clusters of these elements of any kind are currently unknown and the only well characterized stable cationic organo Group 14 cluster is the recently described silyl-substituted germanium species $[Ge_{10}(Si\mathit{t}Bu_3)_6I][B(C_6F_4H)_4]$.[17] Herein we report three new element-rich organo clusters of tin whose structures are analogous to, or derived from, the E_9^{x-} Zintl framework. These are the neutral $Sn_9(Ar^{Trip_2})_3 \cdot 4\,THF$ (**1**·4 THF; $Ar^{Trip_2} = 2,6\text{-}(2,4,6\text{-}\mathit{i}Pr_3C_6H_2)_2C_6H_3$) and the cationic clusters $[Sn_{10}(Ar^{Mes_2})_3]$ $[AlCl_4]$·PhMe (**2**·PhMe) and $[Sn_{10}(Ar^{Mes_2})_3][GaCl_4]$·PhMe (**3**·PhMe).

The neutral cluster $Sn_9(Ar^{Trip_2})_3$, which is paramagnetic and has 21 framework electrons, was synthesized by the thermolysis of $\{Ar^{Trip_2}Sn(\mu\text{-}H)\}_2$[18] in hot toluene and was isolated as dark red, almost black crystals. This method is a new synthetic route to tin clusters[19] that arose from exploring

[*] Dr. A. F. Richards, Dr. B. E. Eichler, Dr. M. Brynda, Prof. M. M. Olmstead, Prof. P. P. Power
Department of Chemistry, University of California
One Shields Avenue, Davis, CA 95616 (USA)
Fax: (+1) 530-752-8995
E-mail: pppower@ucdavis.edu

[**] The authors thank the NSF-CRC program for financial support. M.B. was supported by the Swiss National Science Foundation Grant 8220-067593.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  DOI: 10.1002/ange.200500117

the decomposition of the hydride in an attempt to isolate the distannyne $Ar^{Trip_2}SnSnAr^{Trip_2}$.[20] Elimination of hydrogen does occur, but competing Sn–C bond cleavage results in ligand stripping to afford **1**. The arene HAr^{Trip_2} was also isolated from the reaction mixture. Compound **1** was characterized by X-ray crystallography and by EPR spectroscopy. The latter afforded a relatively broad signal with a *g* value near 2.031 in solution in toluene at room temperature. A representation of the structure of **1**[21] is shown in Figure 1. The Sn_9 framework

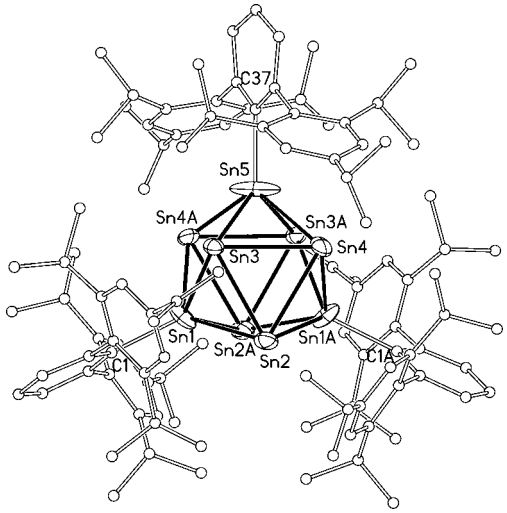

Figure 1. Schematic drawing of **1**. Selected bond lengths [Å] and angles [°]: Sn1-C1 2.21(2), Sn1-Sn2 2.944(2), Sn1-Sn3 2.967(2), Sn1-Sn4A 2.912(2), Sn2-Sn3 2.992(2), Sn2-Sn4 3.008(2), Sn3-Sn4 2.999(2), Sn3-Sn5 2.914(2), Sn4-Sn5 2.932(2), Sn5-C37 2.21(3); C1-Sn1-Sn2 122.9(4), C1-Sn1-Sn3 119.5(4), C1-Sn1-Sn4A 116.0(4), Sn2-Sn3-Sn4 60.27(4), Sn3-Sn2-Sn4 59.98(4).

has a tricapped, trigonal-prismatic, closo structure, which is similar to that first reported for the 21-framework-electron Zintl ion $[Sn_9]^{3-}$ by Corbett in 1983.[22] The most prominent structural features of trigonal-prismatic clusters of this type concern the Sn–Sn separations that define the height (h) and edge (e) of the trigonal prism and the distance from the capping to prismatic atoms.[23] In **1**, the average values for these distances are h = 4.12(4), e = 3.000(1), and capping distance 2.94(3) Å, respectively. These parameters afford an h/e value of 1.37, which is significantly higher than the range currently known (1.07–1.17) for $[E_9]^{3-}$ Zintl ions with 21 framework electrons.[2] The h/e value is closest to that recently observed for the anionic substituted germanium cluster $[Ge_9\{N(SiMe_3)_2\}_3]^-$ (h/e = 1.27),[11] which also has a closo structure despite the fact that it has 22 framework electrons for which a nido, monocapped square-antiprismatic arrangement is predicted by Wade's rules. Calculations[11] on the model species $[Ge_9H_3]^-$, however, yielded structural parameters close to those experimentally observed. In contrast, the derivatized Zintl ion $[Ge_9(BiPh_2)_2]^{2-}$[14] displays a nido Ge_9 framework that is consistent with its 22 framework electrons. The Sn–Sn bond length pattern in **1** is similar to that seen in closo $[E_9]^{3-}$ Zintl clusters where the shortest bonds (Sn–Sn bond lengths in the range 2.914(2)–2.967(2) Å) are observed to the tin atoms capping the rectangular prism faces, that is, the substituted Sn1, Sn1A, and Sn5 in **1**. DFT calculations[24] for Sn_9Me_3 model species for **1** afforded Sn–Sn bond lengths that resemble those experimentally observed, with the lengths calculated for the four-coordinate tin centers (average 2.935 Å) falling within the above-mentioned range. The calculated h/e value, 3.83 Å(avg)/3.25 Å(avg) ≈ 1.18 is not as great as that seen in **1**. However, it is greater than that in the $[Sn_9]^{3-}$ Zintl ion (h/e = 1.08).[22]

The cluster salts **2** and **3** were synthesized by the reduction of $Sn(Cl)Ar^{Mes_2}$ with one equivalent of KC_8 in the presence of 0.5 equivalents of $AlCl_3$ or $GaCl_3$. This synthetic approach arose out of attempts to isolate clusters with both Group 14 and Group 13 atoms in their frameworks. The inclusion of Group 13 elements was successful with use of the subvalent gallium (I) precursor "GaI",[25] but the use of $M^{III}Cl_3$ (M = Al or Ga) halides has not afforded "mixed" clusters to date. The products **2** and **3** were obtained as red–black hexagonal crystals. Although these crystals have a relatively high melting point, attempts at redissolving them result in decomposition with the deposition of elemental tin. Single-crystal X-ray diffraction established the structure that is illustrated for **2** in Figure 2. The Sn_{10} framework in the $[Sn_{10}(Ar^{Mes_2})_3]^+$ ion is almost identical in both compounds and the structure is based on a distorted octadecahedron. It may be viewed as being composed of Sn^{2+} ions (Sn5) capping Zintl-like $[Sn_9(Ar^{Mes_2})_3]^-$ moieties which are related to the neutral species **1** by a one-electron reduction. The existence of such monoanionic Zintl-like ions has precedence in the above-mentioned $[Ge_9\{N(SiMe_3)_2\}_3]^-$ ion.[16] The framework electron count for the Sn_{10}

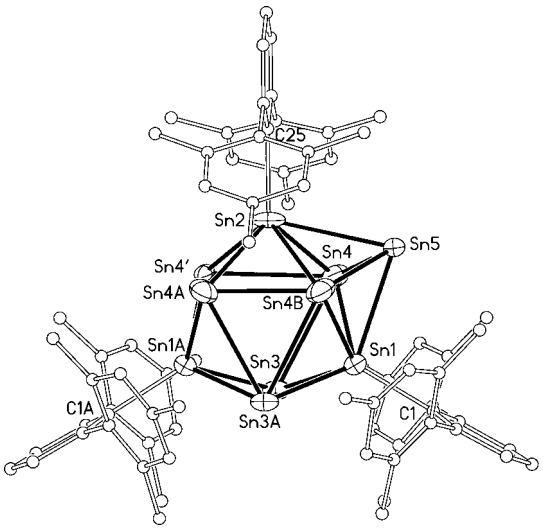

Figure 2. Schematic drawing of the cation in **2** (that in **3** is almost the same). Selected bond lengths [Å] and angles [°]. Sn1-C1 2.194(11), Sn2-C25 2.198(12), Sn1-Sn3 2.9174(8), Sn1-Sn4 3.010(1), Sn1-Sn5 3.000(1), Sn2-Sn5 3.118(1), Sn2-Sn4 3.122(1), Sn3-Sn4 3.087(1), Sn4-Sn5 2.9552, Sn4A-Sn4B 2.8929(2), Sn4-Sn4′ 3.185(2); C1-Sn1-Sn3 112.7(3), C1-Sn1-Sn4 115.2(3), Sn3-Sn1-Sn4 61.64(3), Sn4-Sn1-Sn5 57.91(3), Sn3-Sn1-Sn4 61.64(3), Sn4-Sn1-Sn5 57.91(3), Sn4-Sn1-Sn4B 96.14(5), C25-Sn2-Sn5 102.70(3), Sn4-Sn2-Sn5 56.52(2), Sn4A-Sn2-Sn4B 53.87(4), Sn4-Sn2-Sn4′ 65.22(6), Sn1-Sn3-Sn4 62.09(3), Sn1-Sn4-Sn5 61.66(3), Sn4′-Sn4-Sn5 114.45(3), Sn1-Sn5-Sn4 67.74(3), Sn2-Sn5-Sn4 61.82(3), Sn1-Sn5-Sn2 83.84(4).

cation is 22, which is agreement with the view that it is derived from monocapping of the original trigonal-prismatic $Sn_9(Ar^{Mes_2})_3$ unit by a tin atom. This capping causes large distortions of the original trigonal-prismatic arrangement seen in the structures of **1** and the $[Ge_9\{N(SiMe_3)_2\}_3]^-$ ion. The original parallel trigonal Sn3 faces of the prism, which were separated by a relatively uniform "height" of approximately 4.0 Å between the respective pairs of tin atoms in **1**, become separated by 3.824, 3.946, and 4.594 Å in **2**; the longest distance (between Sn4 and Sn4B) in **2** is now bridged by the capping Sn5. Elsewhere within the cluster the Sn–Sn bond lengths are within the range 2.760(2)–3.185(2) Å.

In conclusion, we have isolated and characterized two new types of organotin clusters that are related structurally to the Sn_9^{x-} Zintl anions. The isolation of these compounds strengthens the notion that clusters of Group 14 elements can demonstrate a great variety of structural types and firmly establishes a relationship between the Zintl and organo clusters. The results suggest that further capping of the Sn_9^{x-} framework should lead to higher clusters. In addition, the ability of the terphenyl ligands to stabilize **1**–**3** as well as other clusters in which the majority of the metal atoms are unsubstituted[9] is noteworthy.

Experimental Section

All manipulations were carried out under an inert atmosphere in water-free conditions.

1: $\{Sn(\mu\text{-}H)Ar^{Trip_2}\}_2$ (0.601 g, 0.5 mmol) in toluene (30 mL) was heated to 100 °C in an oil bath for 1 h, during which time the initial blue color of the solution became dark red. The solution was cooled and filtered. The volume of the filtrate was reduced to saturation, but attempts to grow crystals for X-ray diffraction from toluene solutions were unsuccessful. With the addition of small quantities (ca. 5% volume) of THF, crystals of **1**·4 THF suitable for X-ray studies were obtained as red needles (0.052 g, 19%); m.p. desolvates at ca. 80°, dec > 100 °C. Elemental analysis (%) calcd for $C_{108}H_{147}Sn_9$: C 51.64, H 5.90; found: C 52.16, H, 6.03.

2: A solution of $Sn(Cl)Ar^{Mes_2}$ (0.467 g, 1 mmol) and $AlCl_3$ (0.67 g, 0.5 mmol) in THF (20 mL) was added dropwise to a well-stirred suspension of KC_8 (0.135 g, 1 mmol) in THF (20 mL) cooled in a dry-ice/acetone bath. The solution was allowed to reach room temperature within 12 h and filtered. The filtrate was collected, the volatile materials were removed under reduced pressure, and the residue was extracted with toluene (30 mL) and filtered. The filtrate was reduced in volume to incipient crystallization and stored at room temperature for one week to afford **2** as black (dark red in transmitted light) hexagonal crystals. (0.028 g, 12%); m.p. 144–146 °C. Elemental analysis (%) calcd for $C_{72}H_{75}Cl_4AlSn_{10}$: C 37.66, H 3.29; found: C 38.10, H 3.34.

3: The preparation of **3** was almost identical to that for **2** except that $GaCl_3$ was employed instead of $AlCl_3$. The product **3** was obtained as black (dark red in transmitted light) crystals (0.023 g, 10%); m.p. 185–186 °C. Elemental analysis (%) calcd for $C_{72}H_{75}Cl_4GaSn_{10}$: C 36.97, H 3.32; found: C 37.61, H 3.29.

Received: January 12, 2005
Published online: March 22, 2005

Keywords: cluster compounds · density functional calculations · structure elucidation · tin

[1] J. D. Corbett, *Angew. Chem.* **2000**, *112*, 682; *Angew. Chem. Int. Ed.* **2000**, *39*, 670.
[2] T. F. Fässler, *Coord. Chem. Rev.* **2001**, *215*, 347.
[3] A. Sekiguchi, S. Nagase, *The Chemistry of Organic Silicon Compounds*, *Vol. 2*, Part 1 (Eds.: Z. Rappaport, Y. Apeloig), Wiley, Chichester, **1998**, chap. 3, pp. 119–152.
[4] N. Wiberg, P. P. , Power, *Molecular Clusters of the Main Group Elements* (Eds.: M. Driess, H. Nöth), Wiley-VCH, Weineim, **2004**, chap. 25, pp. 188–208.
[5] A Schnepf, *Angew. Chem.* **2004**, *116*, 680; *Angew. Chem. Int. Ed.* **2004**, *43*, 664.
[6] N. Wiberg, H.-W. Lerner, S. Wagner, H. Nöth, T. Seifert, *Z. Naturforsch. B* **1999**, *54*, 877.
[7] B. E. Eichler, P. P. Power, *Angew. Chem.* **2001**, *113*, 818; *Angew. Chem. Int. Ed.* **2001**, *40*, 796.
[8] A. Schnepf, R. Köppe, *Angew. Chem.* **2003**, *115*, 940; *Angew. Chem. Int. Ed.* **2003**, *42*, 911.
[9] A. F. Richards, H. Hope, P. P. Power, *Angew. Chem.* **2003**, *115*, 4205; *Angew. Chem. Int. Ed.* **2003**, *42*, 4071.
[10] K. W. Klinkhammer, Y. Xiong, S. Yao, *Angew. Chem.* **2004**, *116*, 6328; *Angew. Chem. Int. Ed.* **2004**, *43*, 6206.
[11] B. W. Eichhorn, R. C. Haushalter, *J. Chem. Soc. Chem. Commun.* **1990**, 937.
[12] D. R. Gardner, J. C. Fettinger, B. W. Eichhorn, *Angew. Chem.* **1996**, *108*, 2867; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2852.
[13] J. Campbell, H. P. A. Mercier, H. Francke, D. P. Santry, D. A. Dixon, G. J. Schrobilgen, *Inorg. Chem.* **2002**, *41*, 86.
[14] A. Ugrinov, S. C. Sevov, *J. Am. Chem. Soc.* **2002**, *124*, 2442.
[15] A. Urgrinov, S. C. Sevov, *Chem. Eur. J.* **2004**, *10*, 3727.
[16] A. Schnepf, *Angew. Chem.* **2003**, *115*, 2728; *Angew. Chem. Int. Ed.* **2003**, *42*, 2624.
[17] A. Sekiguchi, Y. Ishida, Y. Kabe, M. Ichinohe, *J. Am. Chem. Soc.* **2002**, *124*, 8776.
[18] B. E. Eichler, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 8785.
[19] The assembly of the Pb_{10} and Pb_{12} clusters in ref. [10] is also believed to proceed through lead hydride intermediates.
[20] L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 11626.
[21] Crystal data for **1**·4 THF, **2**·PhMe, and **3**·PhMe obtained with $Mo_{K\alpha}$ ($\lambda = 0.7107$ Å) radiation at 90 K: **1**: monoclinic, *C*2/*c*, dark red needle, $a = 28.176(2)$, $b = 26.4492(2)$, $c = 16.673(1)$ Å, $\beta = 106.743(1)°$, $V = 11899.6(14)$ Å^3, $Z = 4$, $R1$(obs data) = 0.0826; $wR2$(all data) = 0.2296; **2**: orthorhombic *Cmme*, black hexagonal block, $a = 22.694(2)$, $b = 29.964(2)$, $c = 13.391(1)$ Å, $V = 9105.6(13)$ Å^3, $Z = 4$, $R1$ (obs data) = 0.0608; $wR2$ (all data) = 0.1913; **3**: orthohrombic *Cmme*, dark red block, $a = 22.622(2)$, $b = 29.917(3)$, $c = 13.376(1)$ Å, $Z = 4$, $R1$ (obs data) = 0.0645; $wR2$ (all data) = 0.1816. CCDC-259809–259811 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The structure of **1**·4 THF is disordered with respect to the twofold axis passing through Sn5 and C37. Division of the molecule into two parts was unsuccessful. But only the Sn atoms were assigned anisotropic thermal parameters. The half molecule of 2,6-$Trip_2C_6H_3$ was restrained using the SAME feature of SHELXL which relates its 1,2 and 1,3 positions to those of one-half of the organic moiety. Two molecules of THF are present, in the asymmetric unit. The molecules **2**·PhMe and **3**·PhMe are isostructural and were solved in the space group *Cmme* (No. 67, formerly *Cmma*). They consist of the cation $[R_3Sn_{10}]^+$ at a crystallographic site with mm symmetry, the anion $[AlCl_4]^-$ or $[GaCl_4]^-$ at a site of 222 symmetry and disordered PhMe at a site of 2/*m* symmetry. The anion is fully ordered, and PhMe was refined as a rigid group at the multiplicity of the site (0.25

occupancy) with isotropic thermal parameters. In the cation, there are two anomalies which lower the symmetry of the cluster. One of the Sn atoms (Sn5) is clearly at half occupancy and Sn4 occupies two sites in the ratio Sn4:Sn4′:0.75:0.25, which was established by refinement. The three atoms Sn4, Sn4A, and Sn4B are symmetry-related positions for the major atom of the site shared by Sn4 and Sn4′. The minor atom, Sn4′, is drawn such that it occupies the side of the cluster where Sn5 is absent to avoid unrealistically short bonds. In the average structure, Sn4′ would occupy all four positions related by *mm* symmetry, and Sn5 (which resides on a mirror plane) would be reflected to the opposite side as well. These various distortions in the cluster may be the cause of disorder in the R group beginning with the atom C1. The atoms that make up this group are disordered with respect to a mirror plane that passes through the *ipso* carbon C1 and the *para* carbon C4 of the C1 aryl ring. This gives the appearance of large thermal motions perpendicular to this plane. To better describe this group, the atoms C1 and C4 were shifted off the mirror and the remainder of the atoms in this group located from a difference Fourier map. Thus, the atoms C1–C24 were refined at 0.5 occupancy with isotropic thermal parameters and a SHELXL PART-1 statement.

[22] S. C. Critchlow, J. D. Corbett, *J. Am. Chem. Soc.* **1983**, *105*, 5715.

[23] T. F. Fässler, U. Schutz, *Inorg. Chem.* **1999**, *38*, 1866.

[24] The geometry optimizations of the model tin clusters Sn_9Me_3 and $[Sn_{10}Me_3]^+$ were performed using DFT with a hybrid B3LYP functional, including Becke's three-parameter nonlocal exchange potential and the nonlocal correlation functional of Lee–Yang–Parr . To reduce the computational costs without neglecting the relativistic effects, the effects of the core electrons on valence shell for Sn were represented by the quasi-relativistic effective-core potentials (ECPs). For this purpose two ECPs were used for tin atoms: Los Alamos LanL2DZ pseudopotential ECP with a valence basis (Sn 46 electrons core ECP, plus contracted (3s,3p)→[2s,2p]) and the large core CRENBL ECP augmented with polarization functions for C and Sn. Final optimization was also performed with an all electron 3-21g* basis set. The DFT calculations were carried out using the GAUSSIAN 03 package and the representations of the molecular structures and molecular orbitals were generated with the MOLEKEL program. The optimized geometrical parameters (interatomic distances [Å] and angles [°]) vary slightly with the basis set size; the Sn–Sn bond lengths are shorter by an average of 0.05–0.07 Å in the structure optimized at B3LYP/3-21g* level compared to the structure optimized using ECPs. These parameters obtained at B3LYP/3-21g* for Sn_9Me_3 and $[Sn_9Me_3]^+$ are in good agreement with those found in the crystal structure of **1** and **2**. Model of **1**, Sn_9Me_3: Sn1-Sn2 2.937, Sn1-Sn2A 2.937, Sn1-Sn3 2.935, Sn1-Sn4A 2.937, Sn2-Sn3 3.262, Sn3-Sn4 3.247, Sn2-Sn4 3.254; torsion angle Sn1A-Sn3A-Sn4-Sn5 33.4. Model of **2**, $[Sn_9Me_3]^+$: Sn1-Sn5 2.965, Sn1-Sn3 2.979, Sn1-Sn4 3.108, Sn4···Sn4B 4.852; Sn3-Sn1A-Sn4 69.4, Sn1-Sn3-Sn3A 50.8, Sn1-Sn4-Sn2 76.8, Sn1-Sn5-Sn2 81.3. Other relevant bond lengths and angles from the optimized structures are listed in the Supporting Information.

[25] A. F. Richards, M. Brynda, P. P. Power, *Organometallics* **2004**, *23*, 4009.

